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SOLID THERMOSETTING COATING COMPOSITION  
[NETSUKOKASEI KOKEI HIFUKUYO SOSEIBUTSU]

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## 1. Title of the Invention

Solid Thermosetting Coating Composition

## 2. Claim(s)

1. A solid thermosetting coating composition characterized by comprising a combination of at least one of a polyvalent epoxy compound and a polyvalent carboxyl compound, which are film-formable polymers, or a film-formable compound simultaneously having an epoxy group and a carboxyl group, and ammonia or an organoamine; and at least a carboxyl group being contained by forming a salt with ammonia or an organoamine.

## 3. Detailed Specifications

The present invention relates to a solid thermosetting coating composition, and in further detail, a solid thermosetting coating composition having satisfactory storage stability and able to provide a paint having outstanding smoothness, thermal stability, glossiness, solvent resistance, weatherability and impact resistance.

Organic solvent paints, water-soluble paints, emulsion paints or solvent-free paints diluted with a reactive diluent have been used mainly with coaters for coating metals and the like. However, in recent years, solid coating compositions mostly or completely free of volatile constituents, such as solvents and water, have been developed and are being put to practical use. Many vinyl chloride resins and epoxy resin have been used for the resin constituent of such solid coating compositions, and most recently, solid thermosetting coating compositions using

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\*Number in the margin indicates pagination in the foreign text.

thermosetting polyester resins and acrylic resins have been especially investigated for providing paints having outstanding thermostability, weatherability and pressure-sensitive adhesion. Of these solid thermosetting coating compositions, curing, e.g., epoxy resin-based solid thermosetting coating compositions by using a compound having a functional group (e.g., carboxyl group and phenolic hydroxy group) reactable with the epoxy group, or an amine is usually performed. In addition, a thermosetting polyester resin- or acrylic resin-based solid thermosetting coating composition uses at least one kind of monomer having a functional group during synthesis of this resin, and it is cured by using a compound having a functional group reactable with this functional group. For example, a compound having an active methylol group or isocyanate group is /170 wholly used for the hydroxyl group, a compound having a hydroxyl group or epoxy group is wholly used for the resin having a carboxyl group, and an amine or a compound having a carboxyl group or acid anhydride group is wholly used for the resin having an epoxy group.

The chemical reactivity of any of the various functional groups of the above-mentioned resins of such solid thermosetting coating compositions tends to be high and a chemical bond tends to form easily by a reaction with another functional group. In particular, the reaction rate of a combination of an epoxy group and a carboxyl group or amino group is extremely high; hence, the coated powder particles are completely melted with heat, and before a smooth film is formed, a crosslinking reaction proceeds. As a result of the flow on the paint surface being inhibited, it was difficult to obtain a sufficiently smooth paint.

It is generally known that fusion between the powder particles and a so-called blocking phenomenon arises during storage of a solid coating composition, and this phenomenon is referred to as a state in which the powder particle surface has tackiness and the powder particles coalesce with each other. Depending on the extent of such a phenomenon, the concerned composition cannot be put to practical use as a powder paint yet. For example, in the case combinations of an epoxy group and an amino group, the majority of compounds having an amino group and a so-called amine are liquids, and even if they are solids, the melting point is low; hence, the aforementioned blocking phenomenon readily occurs and a powder paint comprising this combination in the past could not be put to practical use.

Furthermore, since a powder paint comprises solid particles, the storage stability is usually better than that of a solvent-based paint. However, during storage, a crosslinking reaction with a conventional powder paint proceeds gradually within the particle solid phase. As a result, when it is stored for a long period, the paint deteriorates and a smooth paint film cannot be obtained.

As a result of repeated research for the purpose of eliminating the aforementioned drawbacks of such solid thermosetting coating compositions, the inventors of the present invention discovered that just three combinations of an epoxy group, a carboxyl group highly reactive with it, and an amino group could be used as the functional groups of the constituents composing the concerned composition. By employing these three combinations, it is confirmed that the carboxyl group and amino

group form a relatively stable salt under temperature conditions normally employed in the manufacture of the concerned composition. As a result, it is thought that a crosslinking reaction of an epoxy group cannot easily arise, and the storage stability of the concerned composition is improved. The heat fluidity of the concerned composition comprising such functional groups is satisfactory and a smooth paint film is obtained. It is thought this is because the above-mentioned salts dissociate in the carboxyl group and amino group at first under the temperature conditions of baking and curing normally employed, and after that, they respectively undergo a crosslinking reaction with the epoxy group.

The present invention was completed on the basis of the above findings, and is characterized by comprising a combination of at least one of a polyvalent epoxy compound and a polyvalent carboxyl compound, which are film-formable polymers, or a film-formable compound simultaneously having an epoxy group and a carboxyl group, and ammonia or an organoamine; and at least a carboxyl group being contained by forming a salt with ammonia or an organoamine.

The constitution and modes of the composition of the present invention will be described in further detail as follows.

(1) A constitution in which the composition may be composed of a combination of a polyvalent epoxy compound and a polyvalent carboxy compound, which are the main film-forming polymer constituents, and a salt is formed by binding ammonia or an organoamine with a carboxyl group. Consequently, during startup, it can be composed of a polymer polyvalent epoxy compound, a polyvalent carboxyl compound, and ammonia or an organoamine.

(2) A constitution in which the composition comprises a combination of a polyvalent epoxy compound and a polyvalent carboxyl compound, which is the main film-formable polymer constituent, to similarly form a salt as in (1) above. As a consequence, during startup, it may be a constitution having the same meaning as in (1) above.

(3) A constitution in which both the polyvalent epoxy compound and polyvalent carboxyl compound are film-formable polymer constituents, and the carboxyl group forms a salt as in (1) above. Therefore, during startup, it may be a constitution having the same meaning as in (1) above.

(4) A constitution in which the composition comprises a film-formable polymer compound simultaneously having an epoxy group and a carboxyl /171 group and the carboxyl group forms a salt as in (1) above. Consequently, during departure, it may be a constitution having the same meaning as in (1) above.

A vinyl-based copolymer resin having an epoxy group and obtained by copolymerizing one or more polymerizable monomers having a so-called epoxy group, such as glycidyl acrylate, glycidyl methacrylate,  $\beta$ -methylglycidyl acrylate or  $\beta$ -methylglycidyl methacrylate, with at least one other polymerizable monomer is cited for the polyvalent epoxy compound in the present invention. An esterified product of an alcohol having 1 to 16 carbons, an acrylic acid or methacrylic acid (e.g., methyl methacrylate, isobutyl methacrylate, n-butyl methacrylate and n-butyl acrylate), styrene, a styrene derivative, such as  $\alpha$ -methylstyrene or vinyltoluene, a vinyl-based nitrile compound, such as vinyl acetate, acrylonitrile, or methacrylonitrile, and which are polymerizable with the polymerizable monomer having an epoxy

group are cited for the above-mentioned other polymerizable monomers. Such a vinyl-based copolymer resin is a solid at room temperature, and preferably, its glass transition temperature is about 20 to 30°C. It is desirable that the amount of polymerizable monomer having an epoxy group be 5 to 50 wt.%. It is not practical when it is less than 5 wt.% because the weatherability and the mechanical strength, such as the impact resistance, tends to be unsatisfactory since a sufficient crosslinked density is not obtained in the paint film or when it exceeds 50 wt.%, the glossiness of the paint film is reduced.

Furthermore, a so-called epoxy resin is cited for the other polyvalent epoxy compound, which may be a low molecular weight or high molecular weight compound. A bisphenol A, polyalcohol, polyglycol, novolak, alicyclic, halogenated bisphenol, resorcin, bisphenol F, tetrahydroxyphenylethane, glycerin triether and polyolefin types are cited as examples of the type thereof. It is preferable that such an epoxy resin be a solid at room temperature as well, or it be solidified by reacting it partially with another constituent in the composition of the present invention during kneading.

A polyvalent carboxylic acid, such as adipic acid, succinic acid, sebacic acid, 1,10-decane dicarboxylic acid, citric acid, maleic acid, trimellitic acid, dodecenylsuccinic acid, phthalic acid or tetrahydrophthalic acid, is specifically cited for the polyvalent carboxy compound in the present invention when it is provided for use as a film-formable polymer constituent. One or more of these acids may be used therefor. A vinyl-based copolymer resin having a carboxyl group



and obtained by copolymerizing at least one kind of polymerizable monomer (e.g., acrylic acid, methacrylic acid, itaconic acid and crotonic acid) and another polymerizable monomer copolymerizable with these monomers (e.g., the above-mentioned other polymerizable monomer copolymerizable with a polymerizable monomer having an epoxy group) in the usual method is cited when the polyvalent carboxylic compound is provided for use as the film-formable polymer constituent. This vinyl-based copolymer resin is a solid at room temperature, and preferably, the glass transition temperature is about 20 to 30°C or higher. And it is desirable that the amount of polymerizable monomer having a carboxyl group is 3 to 30 wt.%. It is not practical that it be less than 3 wt.% because a sufficient crosslinked density is not obtained and the mechanical strength, such as the solvent resistance, weatherability and impact resistance, tend to be unsatisfactory, or when it exceeds 30 wt.% because the glossiness of the paint film decreases and the surface skin becomes inferior.

Furthermore, a polyester resin and acrylic graft polyester resin, for example, can be used in place of the aforementioned vinyl-based copolymer resin having a carboxyl group. Such a resin also is a solid at room temperature, and the acid number thereof needs to be 30 or more.

A vinyl-based copolymer resin having an epoxy group and carboxyl group and obtained by copolymerizing at least one above-mentioned polymerizable monomer having an epoxy group, at least one above-mentioned polymerizable monomer having a carboxyl group, and at least one polymerizable monomer obtained by copolymerization with these monomers (e.g., the above-mentioned other polymerizable monomer copolymerizable with the

polymerizable monomer having an epoxy group) is cited as an example of the film-formable polymer compound having an epoxy group and carboxyl /172 group in the present invention. This vinyl-based copolymer resin is a solid at room temperature, and preferably, the glass transition temperature is about 20 to 30°C or more, and it is desirable that the amount of polymerizable monomer having an epoxy group and the amount of the polymerizable monomer having a carboxyl group being 5 to 50 wt.% and 3 to 30 wt.%, respectively. It is not practical if either amount is not in the above-mentioned ranges because the paint film performance tends to decrease since the paint film is not obtained with a sufficient crosslinked density, or when each range is exceeded because the glossiness of the paint film decreases and the surface skin becomes inferior.

Ammonia or the organoamine used with or in place of it in the present invention may be well-known per se, and a primary, secondary or tertiary amine, and complexes of these amines are contained in the category thereof.

In particular, the primary or secondary polyvalent amine functions as a crosslinking agent per se; hence, it is not released into the air so its use is advantageous. Aliphatic amine, such as methylamine, ethylamine, dodecylamine, methylamine, diethylamine, dibutylamine, triethylamine, tri-n-butylamine, dimethylethanolamine, triethanolamine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, hexamethylene diamine, dodecamethylene diamine, diethylene triamine, triethylene tetramine or tetraethylene pentamine; and an aromatic amine, such as aminotoluene, xylylene diamine, methaphenylene diamine or diaminotoluene, are exemplified for the above-mentioned primary to tertiary amines.

The above-mentioned ammonia or organoamine may be used individually or as a salt bonded to a carboxyl group in advance, as mentioned above. When a polyvalent carboxylic acid is used as the above-mentioned polyvalent carboxy compound to form such a salt, either of the ammonia or organoamine is neutralized with or without dissolving it in a solvent (e.g., tetrahydrofuran), and the resulting salt should be isolated and purified. When the vinyl-based copolymer resin having a carboxyl group is used, the resin obtained by acting ammonia or an organoamine on the polymerizable monomer having a carboxyl group before copolymerization, or by copolymerizing these compounds should be mixed with ammonia or the organoamine in a liquid state or molten state. Furthermore, when the copolymer resin having an epoxy group and a carboxyl group is used, it should be melted and mixed with ammonia or the organoamine. When a solution mixing is adopted as the method for forming such a salt, solidification of the salt can be accomplished by applying a reaction solution to a normal spray-drying method or reduced pressure drying method after forming the target salt. When a melt mixing is adopted therefore, a device, such as a hot kneader, extruder, hot roll, cokneader or Henschel mixer, usually used in the manufacture of a solid coating composition should be used. Moreover, a temperature range of 80 to 150°C is preferred for melt mixing. It is not preferable if it exceeds 150°C because the salt thus formed dissociates, and if an epoxy group is present therewith, a crosslinking reaction arises between it and the carboxyl group and/or amino group, and the risk that the constituent system will gel occurs.

When the organoamine used in the composition of the present invention functions as a crosslinking agent as mentioned above, the ratio of the sum of the equivalents of the carboxyl group and organoamine and the equivalent of the epoxy group in the constituent components is preferably range from 1/0.2 to 0.2/1 (it is not practical if this range is deviated from because the glossiness and mechanical strength of the paint film decrease), and that the equivalent ratio of the carboxyl group and organoamine (or ammonia) range from 1/1 to 1/0.1 (it is not preferable that this range be deviated from because if a large amount of organoamine (or ammonia) is used, a blocking phenomenon occurs, which adversely affects the state of the paint film). On the other hand, when the organoamine does not function as a crosslinking agent, it is preferable that the range of the equivalent ratio of the epoxy group and carboxyl group be 1/0.2 to 0.2/1 and that the equivalent ratio of the carboxyl group and organoamine (or ammonia) range from 1/1 to 1/0.1.

By treating a composition comprising such a constitution in the /173 usual melt-mixing method, the composition of the present invention is obtained. Moreover, melt-mixing in this case also is preferably carried out in a temperature range of 80 to 150°C, as mentioned above. Normally, the applicable composition is provided for use after pulverizing it to about 200  $\mu$  or less.

In addition to the aforementioned essential constituents, reactive or nonreactive resins (e.g. melamine-aldehyde resin, urea-aldehyde resin, and benzoguanamine-aldehyde resin), cellulose derivatives, inorganic pigments (e.g., titanium oxide, zinc oxide, silica and carbon black),

organic pigment s(e.g., phthalocyanine blue, phthalocyanine green, permanent red, Hanza yellow and malachite green), and other curing catalysts and surface modifiers used in paints and are compatible with at least one 1 of these constituents normally can be suitably added, as needed, to the composition of the present invention.

The composition of the present invention obtained as mentioned above is coated on various articles to be coated in a powder paint coating method, such as an electrostatic paint method or fluid immersion method, and applied to a baking treatment at the usual conditions (150 to 220°C, 5 to 60 minutes).

According to the composition of the present invention comprising the aforementioned constitution, the carboxyl group and ammonia or an organoamine form a stable salt during storage, and a crosslinking reaction between these and an epoxy group does not arise substantially within the particle solid phase; hence the stability is satisfactory. During baking, the paint film is allowed to sufficiently flow until the above-mentioned salt dissociates, the crosslinking reaction subsequently proceeds, and an extremely smooth paint film is obtained. Furthermore, the epoxy group and the carboxyl group or an organoamine undergo a crosslinking reaction; hence, a paint film having outstanding weatherability, solvent resistance and impact resistance can be obtained.

The present invention is described next by citing practical examples and comparative examples. Moreover, "part(s)" in the practical examples and comparative example mean "weight part(s)."

### Practical Example 1

A polymerization reactor having a stirrer, reflux condenser and thermometer is charged with 30 parts of a 0.5 wt.% aqueous solution of methyl cellulose (trade name: Metholose 60SH-50, made by Shin'etsu Chemical Co., Ltd.) and subsequently, while stirring the interior, a mixed solution comprising 15 parts glycidyl methacrylate, 20 parts methyl methacrylate, 40 parts styrene, 10 parts isobutyl methacrylate, 15 parts n-butyl methacrylate, 1 part t-dodecyl mercaptan and 1 part azobisisobutyronitrile is added, and subjected to a 6-hour suspension copolymerization at a temperature of 70°C to obtain a vinyl-based copolymer resin having an epoxy group. The number average molecular weight of this dried resin was 9,400 and the glass transition temperature was 55°C.

A solution in which 1 mole of hexamethylene diamine was dissolved in 1 kg of tetrahydrofuran was added dropwise gradually to a solution in which 1 mole of sebacic acid was dissolved in 1 kg of tetrahydrofuran under stirring at room temperature to form a white precipitate. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate was a sebacic acid-hexamethylene diamine salt. This precipitate was filtered and dried under reduced pressure to obtain a purified salt.

After dry blending 100 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group, 9.1 parts of the above-mentioned purified salt, and 1 part of the surface modifier, "Modaflow" (trade name, available from Monsanto Chemical Co.), this was melt mixed for 2 minutes at 130°C, and then pulverized using a pulverizer after cooling, a solid

coating composition having a particle size of 150  $\mu$  or less was prepared.

The above-mentioned composition was electrostatically coated to a thickness of 80  $\mu$  on a polished steel plate degreased with a solvent using an electrostatic spray coater for powder coating use, after which this steel plate was baked for 20 minutes at 200°C in a hot drying oven. The appearance of the resulting paint film and the results of performance tests are shown in Table 1. The above-mentioned composition was stored for 6 months at 40°C, a paint film was subsequently formed, as mentioned above, and an evaluation of the appearance was written therewith in Table 1 as the criteria for the storage stability of the above-mentioned composition. Moreover, a decrease in the physical performance was not confirmed and satisfactory. And this was confirmed as in the case of the practical examples hereafter.

#### Comparative Example 1

100 parts of the vinyl-based copolymer resin having an epoxy group obtained in Practical Example 1, 10.6 parts sebacic acid, and 1 part of the surface modifier used in the Practical Example 1 are used to prepare a solid coating composition having a particle size of 150  $\mu$  or less /174 upon treating it at entirely the same conditions as in Practical Example 1.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1, which results are shown in Table 1.

#### Practical Example 2

A mixed solution comprising 15 parts glycidyl methacrylate, 20 parts methyl methacrylate, 40 parts styrene, 5 parts isobutyl methacrylate,

10 parts n-butyl methacrylate, 10 parts n-butyl acrylate, 2 parts t-dodecylmercaptan and 1 part azobisisobutyronitrile was used and subjected to a suspension copolymerization at entirely the same conditions as in Practical Example 1 to obtain a vinyl-based copolymer resin having an epoxy group. The number average molecular weight of this dried resin was 5,400 and the glass transition temperature was 45°C.

1 mole of ethylene diamine and 1 mole of 1,10-decane dicarboxylic acid were dissolved in 1 kg of tetrahydrofuran respectively and these are mixed by the same technique in Practical Example 1 to form a white precipitate. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate was a 1,10-decane dicarboxylic acid-ethylene diamine salt. The above precipitate was filtered and dried under reduced pressure to obtain a purified salt.

100 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group, 4.8 parts 1,10-decane dicarboxylic acid, 4.6 parts of the above-mentioned purified salt and 1 part of the surface modifier used in Practical Example 1 were dry blended, subsequently melt-mixed for 3 minutes at 100°C with a hot roll, then cooled and subsequently pulverized using a pulverizer to prepare a solid coating composition having a particle size of 150  $\mu$  or less.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1 and the results thereof are shown in Table 1.

Comparative Example 2

100 parts of the vinyl-based copolymer resin having an epoxy group and obtained in Practical Example 2, 3.2 parts ethylene diamine and 1



part surface modified used in Practical Example 1 are treated at entirely the same conditions as in Practical Example 2 to prepare a solid coating composition having a particle size of 150  $\mu$  or less.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1 and the results thereof are shown in Table 1.

Practical Example 3

A mixed solution comprising 15 parts glycidyl methacrylate, 43 parts methyl methacrylate, 15 parts isobutyl methacrylate, 5 parts n-butyl acrylate, 3 parts t-dodecylmercaptan and 1 part azobisisobutyronitrile is used and subjected to a suspension copolymerization at entirely the same conditions as in Practical Example 1 to obtain a vinyl-based copolymer resin having an epoxy group. The number average molecular weight of this dried resin was 6,000 and the glass transition temperature was 50°C.

100 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group, 10.8 parts 1,10-decane dicarboxylic acid, 1.1 parts dodecane methylene diamine and 1 part of the surface modifier used in Practical Example 1 are treated at entirely the same conditions as in Practical Example 2 to prepare a solid coating composition having a particle size of 150  $\mu$  or less.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1 and the results thereof are shown in Table 1.

Practical Example 4

A mixed solution comprising 22 parts glycidyl methacrylate, 30 parts methyl methacrylate, 30 parts styrene, 10 parts n-butyl methacrylate, 8 parts n-butyl acrylate, 1 part t-dodecylmercaptan and 1 part

azobisisobutyronitrile is used and subjected to a suspension copolymerization at entirely the same conditions as in Practical Example 1 to obtain a vinyl-based copolymer resin having an epoxy group. The number average molecular weight of this dried resin was 6,700 and the glass transition temperature was 58°C.

70 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group, 10.8 parts 1,10-decane dicarboxylic acid, 1.9 parts dimethylethanolamine, 20 parts titanium oxide, 3.5 parts epoxy resin, "Epon #1001" (trade name; made by Shell Chemical Co.), and 1 part of the surface modifier used in Practical Example 1 were dry blended, subsequently melt-mixed for 1 minute at 100°C with an extruder, then cooled, and subsequently pulverized using a pulverizer to prepare a solid coating composition having a particle size of 150  $\mu$  or less. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate contained a salt. /175

Except for performing the baking conditions for 30 minutes at 160°C using the above-mentioned composition, it is applied to the same test as in Practical Example 1 and the results thereof are shown in Table 1.

Practical Example 5

3 aliquots of a mixed solution comprising 15 parts methacrylic acid, 35 parts methyl methacrylate, 20 parts styrene, 30 parts n-butyl methacrylate, 3 parts t-dodecylmercaptan and 1 part azobisisobutyronitrile are placed in a polymerization reactor having a stirrer, reflux condenser and thermometer, and while stirring the interior, the temperature is raised to 110°C, after which the 7 remaining aliquots of the above-mentioned

mixed solution is added dropwise over 2 hours. 30 minutes after the start of the addition, the internal temperature is raised to 140°C. After the addition is completed, the temperature is maintained at 140°C for 2 hours and a bulk polymerization is completed. By cooling this bulk polymer product, a vinyl-based copolymer resin having a carboxyl group is obtained. The number average molecular weight of this dried resin was 4,000 and the glass transition temperature was 40°C.

75 parts of the above-mentioned vinyl-based copolymer resin having a carboxyl group and 5.45 parts triethylamine melt-mixed for 2 minutes at 100°C with a hot roll, 100 parts of the vinyl-based copolymer resin having an epoxy group obtained in Practical Example 3 and 2 parts of the surface modifier used in Practical Example 1 were added to this, subjected to a melt-mixing for 3 minutes at 100°C with a hot roll to prepare a solid coating composition having a particle size of 150  $\mu$  or less. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate contained a salt.

Except for performing the baking conditions for 20 minutes at 180°C using the above-mentioned composition, it is applied to the same test as in Practical Example 1 and the results thereof are shown in Table 1.

Practical Example 6

After dry blending 100 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group and obtained in Practical Example 5 and 7.6 parts dimethylethanolamine, this was melt mixed for 1 minute at 100°C with a hot roll, 68 parts of the epoxy resin used in Practical Example 4 and 1.2 parts of the surface modifier used in Practical Example

1 were added thereto, melt mixed for 1 minute at 100°C with a hot roll, then cooled and subsequently pulverized using a pulverizer to prepare a solid coating composition having a particle size of 150  $\mu$  or less. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate contained a salt.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1, which results are shown in Table 1.

#### Practical Example 7

A mixed solution obtained by adding 4.8 parts tri-n-butylamine to 1.5 parts methacrylic acid, 35 parts methyl methacrylate, 20 parts styrene, 30 parts n-butyl methacrylate, 1 part t-dodecylmercaptan and 1 part azobisisobutyronitrile is subjected to a suspension copolymerization at entirely the same conditions as in Practical Example 1 to obtain a vinyl-based copolymer resin having a carboxyl group made into the form of a salt. The number average molecular weight of this dried resin was 6,500 and the glass transition temperature was 52°C.

75 parts of the above-mentioned vinyl-based copolymer resin, 100 parts of the above-mentioned vinyl-based copolymer resin having an epoxy group obtained in Practical Example 2, 2 parts melamine resin, "Sumimal M-100" (trade name, made by Sumitomo Chemical Co., Ltd.), and 1 part of the surface modifier used in Practical Example 1 were dry blended, subsequently melt-mixed for 3 minutes at 100°C with a hot roll, then cooled and subsequently pulverized using a pulverizer to prepare a solid coating composition having a particle size of 150  $\mu$  or less. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this

precipitate contained a salt.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1, which results are shown in Table 1.

#### Practical Example 8

66 parts isophthalic anhydride, 13 parts trimethylolpropane, 38 parts neopentylglycol, 15 parts adipic acid and 21 parts methyltetrahydrophthalic acid are reacted for 8 hours at 220°C to obtain a polyester resin having an acid number of 120.

20 parts of the above-mentioned polyester resin are dissolved in a mixture comprising 39 parts methyl methacrylate, 17 parts styrene, 7 parts n-butyl methacrylate, 18 parts glycidyl methacrylate, 2 parts t-dodecylmercaptan and 1 part azobisisobutyronitrile, then 1.5 parts of 28% aqueous ammonia are added and the resulting mixed solution is used and subjected to a suspension copolymerization at entirely the same /176 conditions as in Practical Example 1 to obtain a polyester-modified acrylic resin. The number average molecular weight of this dried resin was 4,800 and the glass transition temperature was 50°C. Upon measuring it with an ultraviolet spectrophotometer, it was confirmed that this precipitate contained a salt.

70 parts of the above-mentioned polyester-modified acrylic resin, 4 parts 1,10-decane dicarboxylic acid, 3 parts of the epoxy resin used in Practical Example 4, 20 parts titanium oxide and 1 part of the surface modifier used in the Practical Example 1 were dry blended, subsequently melt mixed for 1 minute at 100°C with a hot roll, and pulverized using a pulverizer after cooling to prepare a solid coating composition having

a particle size of 150  $\mu$  or less.

The above-mentioned composition is used and applied to the same tests as in Practical Example 1, which results are shown in Table 1.

Table 1

	Practical Example								Comparative Example	
	1	2	3	4	5	6	7	8	1	2
Appearance <sup>(1)</sup>	CC*	CC	CC	CC	CC	CC	CC	CC	x	x
Impact Resistance <sup>(2)</sup>	100	100	100	100	100	100	100	100	100	80
Cross-Cut Tape Method Test <sup>(3)</sup>	100	100	100	100	100	100	100	100	100	80
Solvent Solubility <sup>(4)</sup>	CC	o	o	CC	o	o	CC	CC	o	x
Staining Resistance <sup>(5)</sup>	CC	o	o	CC	o	o	o	o	o	x
Storage Stability <sup>(1)</sup>	CC	o	$\Delta$	o	o	o	o	o	x	x

\*[translator's note: CC is circle in circle]

Notes: (1) The degree of smoothness of the painted surface was judged with the unaided eye according to the following criteria:

CC: extremely satisfactory; o: satisfactory;  $\Delta$ : fair; x: poor.

(2) This was measured at 500 g,  $\frac{1}{2}$  inches, and a height of 30 cm using a Dupont impact testing machine. The state of the splits in the paint film was judged according to the following criteria: CC: abnormal; o: extremely small amount of splits;  $\Delta$ : small amount of splits; x: large amount of splits.

(3) Eleven longitudinal and horizontal cuts were made in the paint film at 1 mm intervals, cellophane tape was pressed thereonto, and peeled to measure the number of remaining squares.

(4) A 1 cm<sup>2</sup> piece of square gauze was impregnated with acetone, set aside on the paint surface for 5 minutes and immediately wiped off. The softened state of the paint film was measured with the unaided eye according to the following criteria: CC: abnormal; o: extremely small amount of softening;  $\Delta$ : small amount of softening; x: large amount of softening.

(5) 5 mm wide, 5 mm long stripes are drawn with three magic markers (red, black and blue), respectively, set aside for 4 hours, after which the stripes are wiped off with a methanol-impregnated gauze. The degree of magic marker stains was judged according to the following criteria: CC: no stain at all; o: very small amount of stain; Δ: small amount of stain; x: large amount of stain.

As seen from Table 1, it is confirmed that the compositions of the present invention (Practical Example 1 to 8) form paint films with far superior glossiness than the conventional compositions (Comparative Examples 1 and 2) and that the storage stability is substantially more satisfactory. It was confirmed that the smoothness, solvent resistance and stain resistance of the paint film obtained from the composition of Comparative Example 2 (epoxy group and amino group combination) were very inferior.